

Method and installation for producing liquid energy carriers from a solid carbon carrier

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Technical field

[1] The invention relates to a process and a plant for producing liquid energy carriers, in particular methanol, from a solid carbon carrier by means of gasification with introduction of external energy and production of a synthesis gas for subsequent syntheses.

[2] The invention is intended, in particular, for use in a compact plant configuration. The liquid energy carriers as final products are energy stores and are intended for mobile or stationary work apparatuses. Such plants utilize, as additional energy, wind power, water power or solar power which have attracted considerable interest in view of limited resources, e.g. in the case of petroleum, and environmental consciousness which has increased recently.

Prior art

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[3] According to the prior art, a large number of processes for producing liquid energy carriers are known. For example, the German "ForschungsVerbund Sonnenenergie", a cooperation of nonuniversity research institutes, is carrying out research with the aim of discovering a lasting energy supply based on new technologies for utilizing renewable energy sources.

[4] In "Methanol-Herstellung und Einsatz als Energieträger für Brennstoffzellen", http://www.fv-sonnenenergie.de/publikationen/th9900/th9900_46-53.pdf J. Pasel et al describe methods of obtaining methanol. Methanol as an alternative fuel for the traffic sector

offers the advantage of a considerable replacement potential for the fuels required today because renewable resources will play an important role in the longer term. Closed material circuits are given as a
5 basic prerequisite for lasting energy systems. Inter alia, fossil raw materials or residues can be gasified with the introduction of energy from wind power, water power or solar power, with the oxygen required for gasification and hydrogen for the synthesis of methanol
10 being produced in a parallel electrolysis.

Description of the invention

[5] It is an **object** of the invention to provide a
15 process for producing liquid energy carriers from a solid carbon carrier of the abovementioned type, which significantly increases the efficiency of such processes. Furthermore, a plant for producing liquid energy carriers from a solid carbon carrier, which has
20 a compact construction and can be utilized for producing fuel for use in work engines for the operation of mobile or stationary work apparatuses, is to be provided.

25 [6] As solid carbon carriers, it should be possible to use, in particular, ones having a reduced heating value, i.e. fossil or recent fuels such as biomass or brown coal which are characterized by a significant natural oxygen content and thus a certain oxidation
30 state and as a result a lower heating value than low-oxygen fuels. Thus, for example, the molar carbon/oxygen ratio in wood is 1:1. The lower energy content resulting therefrom should be compensated by introduction of external energy of nonfossil origin and
35 its storage as chemical energy in the energy carriers to be produced, with the minimization of the external energy consumption being a significant aspect of the object. A further aspect of the object is that the

process should operate without significant process-related carbon dioxide emissions.

[7] The invention achieves the object for the process
5 by means of the features indicated in claim 1 and for
the plant by means of the features in claim 10.
Advantageous embodiments of the invention are
characterized in the respective subordinate claims and
are presented in detail below together with the
10 description of the preferred performance of the
invention, including the drawing.

[8] The central aspect of the invention is the further
development of a process for producing a liquid energy
15 carrier from a synthesis gas in a compact plant by
gasification of a solid carbon carrier. The compact
plant comprises at least a drying apparatus for drying
the carbon carrier, a gasification apparatus for
gasifying the carbon carrier and for producing the
20 synthesis gas, a synthesis apparatus for the synthesis
of the liquid energy carrier from the synthesis gas and
an apparatus for the electrolysis of water for
producing oxygen as gasification agent for the
gasification process in the gasification apparatus and
25 hydrogen for the synthesis process in the synthesis
apparatus.

[9] According to the process, at least part of the
off-vapor from the drying apparatus and at least part
30 of the residual gas obtained in the synthesis is fed to
the gasification process in the gasification apparatus.
The off-vapor increases, in accordance with the thermo-
dynamic water-gas equilibrium, the formation of hydro-
gen and the residual gas, which contains amounts of
35 hydrogen and carbon monoxide, significantly increases
the efficiency of the process.

[10] In one embodiment, the carbon-containing residues

from the gasification apparatus and part of the oxygen produced in the apparatus for the electrolysis of water are fed to the combustion process in a combustion apparatus which is arranged downstream of the gasification apparatus. The CO₂- and oxygen-containing offgas from the combustion apparatus is then advantageously fed as gasification agent to the gasification process in the gasification apparatus.

[11] The drying process for the carbon carrier in the drying apparatus for producing an off-vapor which is free of incondensable components is, in accordance with one embodiment, carried out in a closed system and without entraining air.

[12] The off-vapor from the drying apparatus which is not fed to the gasification process in the gasification apparatus can be condensed in a condenser and utilized externally as heat donor.

[13] In further embodiments, the synthesis gas can be subjected to purification and/or cooling before introduction into the synthesis apparatus and the residues from the gas purification and/or the residual gas from the synthesis apparatus which are not fed to the gasification process in the gasification apparatus can be fed to the combustion process in the combustion apparatus.

[14] The waste heat obtained in the gasification process and/or the synthesis of the liquid energy carrier and/or, if appropriate, the combustion process and/or the gas purification and cooling is advantageously introduced into the drying apparatus.

[15] The inventive combination of the individual streams is overall characterized by introduction of energy of external origin which compensates the energy

deficit corresponding to the natural oxidation state of the carbon carrier used and is present as stored energy in the end product. Recirculation of the residual gases to the product stream ensures virtually complete
5 utilization of the carbon present in the carbon carrier used and an ash which can be deposited in a landfill is obtained.

[16] The generation of additional energy is not a
10 subject matter of the invention. However, in view of the objective to create a process for complete utilization of the carbon carrier and to largely avoid carbon dioxide emissions, this energy should not come from the combustion of fossil or recent fuels.

15 [17] Insofar as it is relevant to the invention, the individual process steps will be briefly explained below.

20 [18] The drying and work-up of the carbon carrier serves to increase the heating value, since this in the original state generally has a high water content and thus a low available heating value, and it is in principle possible to use all known drying methods. The
25 degree of drying is selected as a function of the elemental composition of the carbon carrier and thus its energy content so that the subsequent gasification can be maintained autothermally. Depending on the type of solid carbon carrier used, at least part of the heat
30 energy required for drying can also be taken from the gasification process.

[19] In the embodiment of the invention with a downstream combustion apparatus, the carbon-containing
35 solid gasification residue discharged from the gasification apparatus is reacted with introduction of oxygen to give a gas comprising carbon dioxide and excess oxygen. While a reducing atmosphere prevails in

the gasification process, the combustion process is characterized by an oxidizing atmosphere.

[20] The electrolysis of water to produce hydrogen and oxygen results in electric energy of external origin flowing into the process. The external energy to be introduced compensates the energy deficit of the oxygen-containing carbon carrier and is ultimately transformed into an energy content of the liquid energy carrier and thus converted into a storable form. This means that carbon carriers having a relatively high heating value, e.g. hard coal, can in principle also be processed by means of this process to give liquid energy carriers with storage of the external energy in the liquid products to be produced.

[21] In the gas purification and cooling, the raw gas produced is cooled and brought to the purity required for the synthesis. The cooling of the raw gas produced deserves particular attention since the composition is temperature-dependent because of the Boudouard equilibrium, i.e. in the case of slower cooling, the carbon monoxide present in the gas is increasingly converted into carbon dioxide with deposition of carbon.

[22] For this reason, it is advantageous to carry out cooling in a fluidized-bed apparatus in the plant of the invention. An inert fluidizable material which is fluidized by the gas to be cooled is present in this fluidized-bed apparatus. Owing to the pseudoliquid state of a fluidized bed, this has an almost uniform temperature. When the hot gas from the gasification is fed into the significantly cooler fluidized bed, shock-like cooling occurs and the undesirable conversion of carbon monoxide is avoided as a result.

[23] A heat exchanger in the form of a tube heat

exchanger, plate heat exchanger or other heat exchanger design is integrated into the fluidized-bed apparatus. Boiling water having a pressure which can be chosen freely within certain limits is present in the interior
5 of this heat exchanger so that the heat removed from the hot gas is converted into the corresponding quantity of steam. Owing to the high heat transfer coefficient in the fluidized bed compared to a conventional gas cooler, the heat-exchange area
10 necessary can be reduced by from 70 to 80%. The fluidized-bed apparatus simultaneously functions as a steam generator in which at least part of the heating steam required for drying of the carbon carrier is generated.

15 [24] The fluidized-bed apparatus additionally serves as gas purification stage. As a result of the cooling, the tar and possibly dust present in the raw gas are deposited on the inert fluidizable material. Regeneration
20 tion of the laden fluidizable material is carried out either by continuous or periodic removal of a sub-stream, burning-off of the deposit and recirculation to the fluidized-bed cooler. This regeneration of the inert fluidizable material is advantageously carried
25 out in conjunction with the combustion of the carbon-containing residue from the gasification, as a result of which offgas emission is avoided and the carbon content is utilized. A further cooling step of a conventional type and a fine purification of the gas
30 corresponding to the requirements of the synthesis step can subsequently be carried out.

[25] In the synthesis, the raw gas which has been produced in the gasification and subsequently conditioned
35 is converted into a liquid energy carrier. This synthesis can be, depending on requirements, a hydrocarbon synthesis known per se, e.g. of the Fischer-Tropsch type, a methanol synthesis or another

- synthesis, e.g. an isobutyl oil synthesis. Since the ratio of carbon monoxide to hydrogen required for these syntheses is not present in the raw gas from the gasification when a carbon monoxide conversion is not
- 5 carried out but instead there is an excess of carbon monoxide, the hydrogen requirement is covered by addition of the hydrogen from the electrolysis of water and is set to the carbon monoxide:hydrogen ratio required for the synthesis.
- 10
- [26] Owing to the applicable thermodynamic laws, the known syntheses which have been mentioned above do not proceed completely in the direction of the chosen target product. A residual gas which comprises small
- 15 amounts of unreacted hydrogen and carbon monoxide and also a thermodynamically determined proportion of carbon dioxide from the gasification and inert gas components from the carbon carrier remains.
- 20 [27] The plant of the invention for producing a liquid energy carrier from a synthesis gas comprises at least a drying apparatus for drying the carbon carrier, a gasification apparatus for gasifying the carbon carrier, a synthesis apparatus for the synthesis of the
- 25 liquid energy carrier from the synthesis gas and an apparatus for the electrolysis of water for producing oxygen as gasification agent for the gasification process in the gasification apparatus and hydrogen for the synthesis process in the synthesis apparatus and
- 30 also a combustion apparatus which is connected to the outlet for carbon-containing gasification residues from the gasification apparatus and the oxygen outlet of the apparatus for the electrolysis of water.
- 35 [28] The outlet for the off-vapor from the drying apparatus and/or the outlet for residual gas from the synthesis on the synthesis apparatus is/are connected to the gasification apparatus in one embodiment. In

this way, off-vapor and residual gas from the synthesis can be introduced into the gasification process. At least one device for regulating the amount of off-vapor and/or residual gas is normally also present in this
5 connection.

[29] Furthermore, at least one apparatus for gas purification and/or cooling can be present between the gasification apparatus and/or the synthesis apparatus
10 and/or the combustion apparatus. The apparatus for gas purification and/or cooling can be configured as a fluidized-bed apparatus with integrated steam generation and the outlet for the steam can be connected to an inlet for heating steam on the drying apparatus.

15 [30] The waste heat from the gasification apparatus and/or the synthesis apparatus and/or the combustion apparatus can be collected by means of a waste heat collection apparatus and passed to the drying
20 apparatus.

[31] The advantage of the invention is, in particular, that the electric energy requirement, measured as a proportion of the energy content of the liquid energy
25 carrier produced, can be reduced, e.g. in the case of methanol production from almost 100% to less than 50%, based on the energy content of the methanol produced.

[32] It has been found that combined control of the
30 introduction of the residual gas from the synthesis and the off-vapor from the drying of the carbon carrier enables the overall process to be realized in a largely closed system. The oxygen requirement for the gasification and the hydrogen requirement for the
35 conditioning of the raw gas for the synthesis can be controlled so that the volume ratio is virtually 1:2 and thus corresponds to the formation ratio in the electrolysis of water. As a result, no excess

quantities of oxygen are obtained from the electrolysis.

5 [33] The provision of the electric energy from spontaneously changing natural resources can advantageously be combined with classically produced electric energy, with the major part of the energy always been obtained from wind power, water power or solar power.

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[34] Further advantages are the minimization of the CO₂ output and the virtually pollutant-free residues in the form of neutral ash.

15 **Example**

[35] The invention is illustrated below by means of an example. The associated drawing schematically shows a plant for producing a liquid energy carrier from a solid carbon carrier, including the streams according to the invention.

25 [36] The plant comprises a steam fluidized-bed dryer 1 as drying apparatus for drying the carbon carrier, a fluidized-bed gasifier 2 as gasification apparatus for the gasification of the carbon carrier and for production of the synthesis gas, a synthesis apparatus 3 for the synthesis of the liquid energy carrier from the synthesis gas and an apparatus for the electrolysis of water 4. In addition, a fluidized-bed combustion plant 5 as combustion apparatus and a fluidized-bed cooler 6 as apparatus for gas purification and cooling are present in the specific plant.

35 [37] All units are combined in a compact plant and connected to one another via appropriate lines. The individual streams are explained in more detail below with the description of the process of the invention.

- [38] For example, 4115 kg/h of mechanically prepared raw brown coal **E** having a heating value of 9605 kJ/kg and a water content of 55% by mass are fed as carbon carrier to the steam fluidized-bed dryer 1 and dried there to give 2184 kg/h of dry brown coal **F** having a residual water content of 15.2% by mass and a heating value of 20 250 kJ/kg.
- 5
- [39] The drying step has a heat requirement of 1831 kW. This heat is obtained within the plant in other units and introduced into the drying process. In the example, the heating steam **S** produced in the fluidized-bed cooler 6 as apparatus for gas purification and cooling is utilized.
- 10
- 15
- [40] Under the conditions described by way of example, 1931 kg/h of steam are formed during drying. Of this total amount, 1046 kg/h in a first substream **R** are, according to the invention, fed to the fluidized-bed gasifier 2. A second substream **G** of 885 kg/h is introduced into an off-vapor condenser, with the heat of condensation of 557 kW liberated there being able to be passed as low-temperature heat to an external use.
- 20
- 25
- [41] In parallel to the provision of the prepared solid carbon carrier and also off-vapor from drying for the gasification process, 799 kg/h of oxygen and 115 kg/h of hydrogen are produced from water **A** and introduced external electric energy **B** in the apparatus for the electrolysis of water 4. The electric energy requirement for this is 4.77 MW. In accordance with the objectives of the process, this energy is preferably obtained from water, wind or solar energy plants.
- 30
- 35
- [42] About one third of the oxygen **C** produced electrolytically is fed via stream **C1** to the fluidized-bed gasifier 2 and two thirds are fed via stream **C2** to the

fluidized-bed combustion plant 5. The use of the hydrogen via stream **D** will be explained later.

[43] In the fluidized-bed gasifier 2, a raw gas **H** is
5 produced from the dry brown coal **F** with introduction of
the oxygen via stream **C1**, with, according to the
invention, the streams steam via substream **R** and a
mixture **K** of carbon dioxide and oxygen from the
fluidized-bed combustion plant 5 and a residual gas **O**
10 from the synthesis in which residues of carbon monoxide
and hydrogen from the synthesis apparatus 3 are present
also flowing in. The gasification is carried out at a
mean gasification temperature of 630°C. The residual
gas **O** from the synthesis is introduced in an amount of
15 2369 kg/h.

[44] In the example, purification of the raw gas **H**
finally gives 5658 kg/h of pure gas **M** containing 27.5%
by volume of carbon monoxide and 35.0% by volume of
20 hydrogen. The remainder consists essentially of carbon
dioxide and small amounts of water vapor and methane.

[45] The carbon-containing gasification residue **I** from
the fluidized-bed gasifier 2 and oxygen via stream **C2**
25 are fed into the fluidized-bed combustion plant 5 and
reacted there under an oxidizing atmosphere to give a
mixture **K** of carbon dioxide and oxygen. This gas
mixture **K** is, as mentioned above, fed to the
gasification process in the fluidized-bed gasifier 2.
30 The streams are regulated so that a combustion
temperature of 900°C is maintained.

[46] As waste product of the combustion process, only
the ash **L** which is free of calcium sulfide and
35 consequently does not tend to evolve hydrogen sulfide
in the presence of moisture remains. The ash **L** can
therefore be deposited in a landfill without problems.

[47] The raw gas **H** is purified and cooled in the fluidized-bed cooler 6. An inert fluidizable material is present in the fluidized-bed cooler 6 and is kept in a fluidized state by the raw gas. A tube heat exchanger
5 having a heat-exchange area of about 200 m² and in these tubes boiling water at 191°C and 12.6 bar is present in the operating state dips into the fluidized bed. The usable heat is withdrawn from the raw gas **H** and a stream of steam having the same parameters is
10 produced and is, as mentioned, fed as heating steam **S** to the steam fluidized-bed dryer 1. The fluidized-bed cooling simultaneously acts as gas purification since the condensing tar constituents and dust present in the raw gas are deposited on the inert fluidizable material
15 on cooling of the gas from 630°C to 230°C. The fluidizable material together with the residues from the gas purification **N** can be passed to the fluidized-bed combustion plant 5 for regeneration.

20 [48] If the cooled synthesis gas **M** does not yet meet the requirements of the subsequent methanol synthesis, in particular adherence to the limit values for passage over the catalyst, appropriate measures corresponding to the prior art can be taken.

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[49] In the synthesis apparatus 3, the synthesis gas **M** is then reacted, with the volume ratio of hydrogen:carbon monoxide in the pure gas of about 2.05 required for the synthesis of methanol being ensured by
30 introduction of the hydrogen via stream **D** from the apparatus for the electrolysis of water 4. The synthesis process forms essentially methanol and some by-products such as dimethyl ether and higher alcohols which can remain in the target product crude methanol
35 **Q**.

[50] A residual gas **O** from the synthesis in which residual amounts of carbon monoxide and hydrogen and

also the carbon dioxide present in the synthesis gas and inert gas constituents are present is also obtained in the synthesis process. The residual gas **O** from the synthesis is, as indicated above, fed in an amount of
5 2369 kg/h to the fluidized-bed gasifier 2. A substream of the residual gas is removed from the system in an amount of 1276 kg/h as purge gas **P** in order to avoid accumulation of the inert gas constituents.

10 [51] The overall result of the synthesis process is that raw methanol **Q** is produced in an amount of 1931 kg/h with a chemically bound power of 10 647 kW from 4115 kg/h of mechanically prepared raw brown coal **E**. Based on the power expended for the electrolysis,
15 this is 223%.

List of reference numerals used

- 1 Steam fluidized-bed dryer
- 2 Fluidized-bed gasifier
- 3 Synthesis apparatus
- 4 Apparatus for the electrolysis of water
- 5 Fluidized-bed combustion plant
- 6 Fluidized-bed cooler

Labeling of the streams

- A Water
- B Electric energy
- C Oxygen
- C1 Oxygen of first stream
- C2 Oxygen of second stream
- D Hydrogen
- E Raw brown coal
- F Dry brown coal
- G Off-vapor substream
- H Raw gas
- I Gasification residue
- K Gas mixture
- L Ash
- M Pure gas
- N Residues from gas purification
- O Residual gas from the synthesis
- P Purge gas
- Q Raw methanol
- R Off-vapor substream
- S Heating steam